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(54) METHOD OF MAKING MARKED SURFACES

(71) We, BURMETAL S.A., a French Body Corporate, of Route de Fontenay, 77 Tournan-en-Brie, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of making marked surfaces, and to surfaces so marked.

Surfaces such as those of labels which can be marked by the user are greatly valued for their flexibility of use. Self-adhesive labels of this type are known, which can be used in diverse fields.

In general, such marked labels are produced by manually embossing a deformable plastic at ambient temperature. The embossing causes a permanent disorientation of the molecules which makes the plastic opaque and forms a white relief impression corresponding to the chosen pattern. However, considerable pressure is required which limits the size of the printed patterns which can be obtained, for instance the largest letters that can be printed are of about 8 mm. If it is desired to obtain patterns of greater size, it is necessary to resort to relatively cumbersome apparatuses in order to develop the necessary high pressures, and in any event it is difficult to produce signs or letters with a dimension exceeding 12 mm.

The known labels are generally of complex materials with a relatively thick embossable film, which is required to give an opacity which permits a good contrast effect. Thus, the labels obtained lack flexibility, which makes them difficult to apply to certain supports. Furthermore, the labels obtained can only be used over a restricted temperature without loss of the markings.

Labels are also known where the markings are achieved by hot transfer. However, the patterns of these labels can only be produced under the simultaneous effect of high pressure and high temperatures.

According to the present invention there is provided a method of making marked surfaces, said method comprising the steps of providing a first strip including a support having on at least one face a layer of a pressure sensitive adhesive substance having a grab strength of between 5 and 150 centinewtons/cm which bonds only in response to the application of pressure, placing a second strip including a support having on one face a transferable layer with said transferable layer in contact with but not bonded to said layer of adhesive, positively applying a pressure pattern through one of said strips corresponding to the desired markings whereby upon application of the pressure pattern the transferable layer is stuck to and effectively transferred to the adhesive, and then separating the strips.

The pressure pattern can be applied to the strips either through the first strip or the second strip, with the other strip in each case being applied against a planar support.

If the pressure pattern is applied through the second strip, the support of the first strip can have a layer of adhesive on both faces, one to contact the transferable layer of the second strip, while the other can have a protective film removable after separation of the strips to allow adhesion of the strip to an object. The adhesive on the face of the first strip not in contact with the second strip may be any type of adhesive.

Similarly, if the pressure pattern is applied through the first strip, the support of the second strip can have a layer of adhesive on a face other than that carrying the transferable layer. The adhesive of this layer may suitably be protected by a removable protective film and may be of any type.

The support of the second strip may be of wood or metal if the pressure is applied through the first strip and vice versa. The support of either or both strips can also be transparent, or can be luminescent, iridescent, metallised, printed, pigmented or otherwise coloured.

A protective film may be placed on the layer of adhesive to which the transferable image is adhered in said pattern after separation of the strips. This film may itself have an adhesive layer. Similarly, a protective film or layer may be applied to the transferable layer of the second strip after separation. In both cases, the protective film or layer may have adhesive of any type on its outside, which may itself have a removable cover which is detached before adhering the strip to an object, suitably a transparent object. Clearly the protective film is suitably entirely transparent, but it could also be coloured or patterned if particular effects were required. The protective strip may itself be covered with and adhered to a film having adhesive on both sides, and a further removable release strip may protect the adhesive layer on that side of the film remote from the transferable layer.

The adhesive layer of the first strip can, after separation of the strips, be adhered directly onto a surface, which should suitably be transparent.

Both strips, after separation, and suitably when the respective adhesive and transferable layers are covered, can be used by being introduced into slots or other supports.

On the second strip, a printed pattern is obtained in the transferable layer after separation of the strips. This provides a background which has the colour of the transferable film, with the marking obtained having the appearance and colour of the support. Thus, by varying the appearance, in respect of tone and decoration, of the transferable film and of its support, a considerable variety of products such as panels and labels carrying the desired markings can be produced. For example, a transparent support for the transferable layer can be provided, in which case the printed patterns are themselves transparent and contrast with an opaque background provided by the transferable layer. This process makes it possible, to obtain an infinite variety of printing effects merely by modifying the support.

A considerable variety of products can be obtained by varying the nature of the materials used for the adhesive strip, the support of the transferable layer, the transferable layer and any protective films. Furthermore, the products obtained can show printed patterns whereof the sizes cover a very broad range, because a relatively low pressure suffices for forming and fixing the print.

It has been found that with the method of the invention, a force of the order of 100 kg suffices for cutting and fixing letters of area 9 cm^2, whilst in the case of embossing a polyvinyl chloride film the same force is insufficient to emboss letters of 11 mm height, having an area of 10 to 30 mm^2. The force required to form the prints by embossing is thus 30 to 90 times greater than the force required to form prints by the method of the invention, so it is possible to obtain patterns, signs or letters of large dimensions.

The invention also makes it possible to obtain labels or placards of almost any desired thickness and flexibility. For example it is possible to vary the nature and thickness of the adhesive layer on the first strip and/or the nature and thickness of any transparent covering film without significantly varying the pressure necessary to cause marking.

Furthermore it is possible to provide an infinite range of combinations of greater or lesser contrast by simply varying the colour or appearance of the various components of the strips.

The compositions of the various components can also be chosen to be suitable for their subsequent intended use.

In order to obtain surfaces marked with clear prints by the method of the invention the adhesive layer and the transferable layer should meet certain requirements as follows: the adhesion of the transferable layer to the pressure-sensitive adhesive should only be effective at a particular pressure; this pressure being of the order of that required to be applied to the composite assembly to ensure cutting the printed pattern from the transferable layer. Under simple contact the pressure-sensitive adhesive must have as little affinity as possible for the transferable layer. It is important that after the application of pressure, the parts of the transferable layer surrounding the cut pattern can easily be separated from the adhesive, without being damaged or separated from their support.

It has been found that these conditions are satisfied if the adhesive layers used display the following characteristics:

a low grab strength;
a bond strength which develops only under the influence of positive pressure;
a low tack;
a good internal cohesion; and
a sufficient elasticity.

Each of these points will be amplified below:

(A) The low grab strength is important so that the bond between the transferable layer and the adhesive strip cannot form by simple contact and only becomes effective under the influence of a given pressure; the parts which have not been subjected to the pressure can thus easily be separated. For this purpose adhesive strips can advantageously be used which have a grab strength, measured according to the AFERA standard specifications, of between 5 and 150 centinewtons/cm, and preferably less than 100 centinewtons/cm.

(B) A low tack is necessary so that the non-adhesion of the transferable layer to the pressure-sensitive adhesive when in simple contact with one another, persists over a considerable period of time. The tack must at least be such that the transferable layer when in simple contact with the pressure-sensitive adhesive is not transferred during the time corresponding to at least one cycle of forming the print pattern.

(C) The bond strength which develops under the influence of the pressure must cause the appropriate parts of the transferable layer to become attached to the adhesive strip. Advantageously, the bond strength of the adhesive strip is between 40 and 400 centinewtons/cm.

(D) The internal cohesion determines the permanent anchoring of the adhesive to its support, and this anchoring must not change during any successive operations of the process and in particular during the application of pressure and during the separation of the adhesive strip and the transferable layer.

The internal cohesion must be sufficient to allow the cut pattern to be separated completely by the adhesive strip at the time of separating the strips.

(E) The elasticity must be sufficient for the adhesive to follow possible deformations in the transferable layer during the application of pressure, to permit proper grip of the transferable layer by the adhesive over the entire surface of the cut pattern. The elasticity must also allow the adhesive to follow deformations to which its support is subjected during separation from the transferable layer so as to avoid any accidental transfer to the said transferable layer. The elasticity also plays an important role in the distribution of pressure over the surface of the pattern and this distribution directly affects the quality of cutting. Adhesive compositions which meet the requirements listed above are advantageously chosen from:

I. Adhesives based on polyurethane, prepared from at least one polyol-polyether of high OH number and at least one polyol-polyether of relatively low OH number in such proportions that the average OH number of the mixture is between 50 and 100, a polyisocyanate, a catalyst, and acrylic acid.

This mixture of polyethers contributes to producing a low grab strength and a low tack at the surface, and contributes to producing a relatively high internal bond strength, the effect of which develops under the application of pressure.

II. Adhesives based on silicones crosslinked by peroxides, amines or metal cations, the crosslinking having to be so controlled as to result in the characteristics listed above, and the choice of catalyst being furthermore determined by the conditions of preparation of the adhesive and the conditions under which the support is kept at the working temperatures.

III. Adhesives based on acrylic materials crosslinked by means of peroxides, amines, metal cations and isocyanates.

IV. Adhesives based on polyvinyl ethers.

V. Adhesives based on natural rubbers or preferably on synthetic rubbers, the latter generally allowing adhesives to be obtained which are of better clarity and better stability to ageing of the pattern/adhesive complex formed.

As regards the transferable layer, it must also meet certain requirements so that labels, panels or other articles showing very sharp patterns and impeccable definition are obtained.

In particular the transferable layer may suitably possess a structure which provides it with properties as follows:

I. Sufficient plasticity to allow clean cutting under the effect of pressure without causing jagged edges, tearing or pulling which removes sharpness from the printed pattern.

II. Different elongations of the transferable layer and of its support so as to avoid cutting the support when pressure is applied and to facilitate separation of the support and of the pattern fixed to the pressure-sensitive adhesive.

III. Anchoring properties between the transferable layer and its support which simultaneously ensure good stability of the assembly during the various manipulations, and easy separation of the support and the pattern cut from the transferable layer after it has been fixed to the adhesive.

IV. Sufficient tensile strength to avoid tearing during transportation and during the various operations to which it is subjected.

A transferable layer which meets the various parameters listed above can advantageously consist of a film-forming organic polymer, fillers and/or pigments, to which dyestuffs may or may not be added, and optionally contains plasticisers and/or waxes and/or additive resins differing from the polymer itself.

The adhesion between the transferable layer and the adhesive layer depends on the compatibility between the two.

To ensure prolonged stability of the patterns formed, it is necessary for the products involved in the composition of the transferable layer to be insoluble in the pressure-sensitive adhesive at the use temperatures, so as to avoid any migration.

It has also been found that in addition to the adhesive used, the particle size of any pigments and fillers used has an influence on the adhesive, in the absence of any pressure, between the transferable layer and the pressure-sensitive adhesive. For example, by using fillers and pigments of particle size

between 10 and 100 microns, a film is obtained which has a surface with microprotuberances, which avoid continuous contact between the surface of the transferable layer and the surface of the pressure-sensitive adhesive when the said film is deposited on the said adhesive. This makes it possible to limit the adhesion between the two surfaces and to facilitate their separation.

Under the influence of the pressure applied at the time of forming the pattern, the adhesive is forced to penetrate into all the surface irregularities of the transferable layer, thus producing a close and continuous contact between the adhesive and the cut pattern, and hence resulting in efficient fixing.

Amongst the organic film-forming polymers which can satisfactorily form part of the composition of the transferable layer there may be mentioned: polyvinyl alcohols, polyvinyl ethers, polyvinyl acetates, copolymers of vinyl acetate and vinyl chloride, acrylic materials, nitrocelluloses, cellulose acetates, cellulose acetobutyrates, methyl-celluloses, ethyl-celluloses, carboxymethyl-celluloses, styrene resins, polyurethanes or their mixtures.

The plasticisers are preferably non-migrating and can be chosen from dibutyl phthalate, dicyclohexyl phthalate, dioctyl phthalate, chlorinated diphenyl and chlorinated triphenyl, tricresyl phosphate and polymeric plasticisers such as the polyesters derived from sebacic acid or adipic acid.

These plasticisers are those usually employed for plasticising organic polymers.

The plasticisers are advantageously used in a percentage of 30 to 300% relative to the amount of polymer.

The fillers can be chosen from talcs, dolomites, silica, micas, chalks, titanium oxide, zinc oxide, starches or their mixtures.

The pigments can be inorganic, organic or metallic.

Advantageously, 2 to 11 parts of fillers and/or of pigments can be used per 1 part of polymer.

The support of the transferable layer can consist of a film composed of polymers or copolymers of styrene, polymers or copolymers of olefines, cellulosic derivatives, polyvinyl acetal, polyvinyl esters or halides, polyesters of polycarbonates. The polymers which form the support of the transferable layer can contain a sufficient amount of plasticiser to impart to them the elongation characteristics mentioned above. The support can also consist of a sheet of regenerated cellulose which may or may not be coated with an organic polymer, or of a sheet of paper having a release coating.

The second strip is prepared by coating such a support, by means of known processes, with the components of the transferable layer in the form of a solution, dispersion or molten mass, in such a way that after drying or cooling a film is formed which weighs between 10 and 150 g, per m^2.

The pressure-sensitive adhesive strips used in the process according to the present invention may suitably be those usually sold commercially, but selected to have the required low grab strength and pressure sensitivity and also, advantageously, to agree with the conditions set out below. However, experience has also shown that to remove the printed pattern it is desirable to use a pressure-sensitive adhesive strip whereof the support has a certain flexibility, this flexibility preferably exceeding that of the base support or of the support of the transferable layer.

The optimum such flexibility may be obtained by the use of the following parameters:

The weight per m^2 of the transferable layer, which can be between 5 and 40 g; and the weight per m^2 of the adhesive coating of the pressure-sensitive adhesive strip, which can be between 5 and 30 g on each face of the strip.

The combination of these two parameters determines the application pressure.

All these provisions lead to numerous advantages which can be summarised as follows:

(a) The nature of the adhesive makes it necessary to employ only low pressures in the transfer operation,

(b) the user can make up labels or panels of all types under very practical conditions and/or circumstances involving low cost,

(c) the patterns can be produced and transferred by starting from standard printing characters,

(d) the product is obtained very simply when compared with the known process which consists of forming prints by hot transfer, because heat energy is not used.

The two strips when prepared are superposed with the adhesive in contact with the transferable layer, so as to form a composite assembly. A predetermined pattern for example the letter F as shown in the attached figures, is applied by pressure to this assembly, either from the side of the support of the transferable layer or from the side of the support of the adhesive layer.

The invention will be better understood through the description of some examples of its performance which are given with reference to the attached drawings, in which:

Figures 1 to 4 schematically illustrate a first method according to the invention;

Figure 5 illustrates a variation of the first method;

Figure 6 illustrates a second method according to the invention;

Figure 7 illustrates a variation of the second method;

Figure 8 illustrates a further variation of the second method.

In the following examples, Nos. 1 to 9 describe examples of the method of the invention when the pressure pattern is applied through the strip carrying the transferable material, while Nos. 10 to 13 describe the method when the pressure pattern is applied through the strip carrying the adhesive layer.

EXAMPLE 1.

6 parts of a butyl phthalate are worked into a paste, in a malaxator, with 4 parts of a yellow pigment such as that sold under the trade name of Fast Yellow JN, and 29 parts of a talc passing through an 0.063 mm sieve in the presence of 0.3 parts of a dispersing agent, for example that sold under the trade mark of "Pluronic" L 61.

Thereafter, 57 parts of ethyl acetate and 4 parts of nitrocellulose, such as that sold under the trade name of Nitro-Cellulose E 130, are added. The mixture is malaxated until the nitrocellulose has completely dissolved and the material thus obtained is then spread (Figure 1) by means of a knife on a polyester film 10 of 25 microns thickness, so that after drying a transferable layer 11 weighing 50 g per m^2 is obtained. The transferable layer is thus carried by the polyester film 10 which constitutes its support.

A 50 mm wide strip, for example, is then cut and a transfer strip marked overall as 12 is obtained. The transfer strip 12 is placed on one of the adhesive faces 14, 15 of a double-sided pressure-sensitive adhesive strip 13 (Figure 2), 50 mm wide, having the required grab strength and pressure sensitivity properties and having a support based on transparent polyvinyl chloride, the transfer strip being placed in such a way that the transferable layer 11 faces the adhesive layer 14 and its support 10 hence faces outwards.

A character 16, representing a letter of 35 mm height and about 630 mm^2 surface area, is then placed on the support 10, and a force of 70 kg is applied to this letter, giving a pressure of about 11 kg/cm^2. The application of this pressure makes it possible simultaneously to cut from the transferable layer a pattern corresponding to the letter and to fix this pattern to the pressure-sensitive adhesive 14. The character may be of a plastic metal such as lead. The character is then withdrawn and thereafter (Figure 3) the support 10 and the non-fixed part of the transferable layer 11 are removed.

The transferred pattern M thus appears as the transfer strip is removed.

The strip obtained is covered (Figure 4) with a protective coating consisting of a strip 19 of transparent polyester, 50 mm wide and 25 microns thick.

Depending on the particular case, a pressure-sensitive adhesive label or placard is thus obtained which is very flexible and carries a very sharp and very luminous yellow print on a transparent background.

In use, the non-stick strip 18 on the second adhesive layer 15 is simply lifted off in order to apply the product to a suitable surface.

EXAMPLE 2.

7.5 parts of dioctyl phthalate are worked into a paste, in a malaxator, with 18 parts of a talc passing through an 0.063 mm sieve and 8 parts of titanium oxide passing through an 0.063 mm sieve, in the presence of 0.3 part of a dispersing agent, for example that sold under the trade name of Pluronic L 61. Thereafter 3 parts of ethylcellulose, such as that sold under the trade name of Ethyl-Cellulose, N 300, and 56 parts of methyl ethyl ketone, are added.

The whole is malaxated until the ethylcellulose has dissolved completely, and the material thus obtained is then applied by means of a knife to a 25 microns thick polyester film so that after drying a transferable film weighing 30 g per m^2 is obtained. The transferable film is thus carried by the polyester film which constitutes its support.

A 19 mm wide strip is then cut so as to give a transfer strip.

The transfer strip so obtained is placed on one of the adhesive faces of a double-sided pressure-sensitive adhesive strip 19 mm wide, having the required grab strength and pressure sensitivity properties and having a support consisting of red "Cellophane" (Trade Mark) in such a way that the transferable film faces one layer of adhesive, its support facing outwards.

A character as in Example 1 and representing a numeral 10 mm high and of about 500 mm^2 surface area is then placed on the support of the transferable layer. A force of 55 kg is applied to the said character, giving to it a pressure of about 11 kg/cm^2. Cutting of a pattern corresponding to the numeral from the transfer strip, and fixing of the said numeral pattern to the pressure-sensitive adhesive, thereupon take place simultaneously. After withdrawing the character, the support of the transferable layer is removed, still bearing the non-fixed parts of the film.

The printed strip obtained is then covered with a pressure-sensitive adhesive strip, such as those sold commercially, 10 mm wide and having a support consisting of colourless and transparent "Cellophane" (Trade Mark). The adhesive strip is so arranged that the adhesive face comes into contact with the print.

A pressure-sensitive adhesive label is thus obtained which is of very pleasant appearance, shows a white print on a red background, and is so flexible that it can be applied to any support.

EXAMPLE 3.

11.3 parts of a polyester derived from sebacic acid, such as that sold under the trade name of Garbeflex HM 10 (a sebacic acid polyester) is worked into a paste, in a malaxator with 32 parts of chalk passing through a 0.063 mm sieve, 2 parts of a black dyestuff such as that sold under the trade name of "Black 842" and 0.3 parts of a dispersing agent such as that sold under the trade name of Pluronic L 61.

Thereafter, 12 parts of a copolymer of vinyl acetate and vinyl chloride, such as that sold under the trade mark of "Rhodopas" AX (a vinyl chloride acetate copolymer), and 44 parts of methyl ethyl ketone, are added. The whole is malaxated until the copolymer of vinyl acetate and vinyl chloride has dissolved completely, and the material thus obtained is then applied by means of a knife to a 25 microns thick polyester film so that after drying a transferable layer weighing 40 g per m^2 is obtained.

The transferable layer is carried by the polyester film, which thus forms the support.

A 12 mm wide strip is cut and a transfer strip is thus obtained.

The transfer strip obtained above is applied to one of the adhesive faces of a double-sided pressure-sensitive adhesive strip 12 mm wide having the required low grab strength and pressure sensitivity properties and having a support consisting of yellow cellulose acetate, in such a way that the transferable layer faces the adhesive, its support thus facing outwards.

A characer of the type previously described and representing a letter 6 mm high and of about 13 mm^2 surface area is now placed on this support. A force of 12 kg is applied to the said character, causing the cutting and fixing of a pattern of transferable layer corresponding to the said letter, and the support of the transferable layer and the non-fixed parts of this film are then removed, after having withdrawn the character.

The printed strip obtained is now covered with a transparent 12 mm wide strip of cellulose acetate. A pressure-sensitive adhesive label showing black prints on a yellow background is thus obtained.

EXAMPLE 4.

10 parts of a butyl phthalate are worked into a paste, in a malaxator, with 2 parts of carbon black such as, for example, that sold under the trade name of "Carbon Black BL" and 31 parts of a talc passing through an 0.063 mm sieve, in the presence of 0.3 part of a dispersing agent, for example that sold under the trade name of Pluronic L 61.

Thereafter, 52 parts of methyl ethyl ketone, 2.85 parts of ethyl cellulose, such as that sold under the trade name of Ethyl-Cellulose N 300 and 0.5 part of polyvinyl acetate, such as that sold under the trade name of Rhodopas M are added. The whole is malaxated until the ethyl cellulose and the polyvinyl acetate have dissolved completely, and the material thus obtained is then applied by means of a knife to a 25 microns thick polyester film so that after drying a transferable layer weighing 50 g per m^2 is obtained. The transferable layer is thus carried by the polyester film which forms its support.

A 50 mm wide strip is now cut and a transfer strip obtained.

The transfer strip is applied to the adhesive face of a single-sided pressure-sensitive adhesive strip, 50 mm wide having the required grab strength and pressure sensitivity properties and having a 50 microns thick polyvinyl chloride support coloured white, in such a way that the transferable layer faces the adhesive, its support thus facing outwards.

A character as before and representing a letter 35 mm high and of about 630 mm^2 surface area is now placed on this support, and a force of 70 kg, corresponding to a pressure of about 11 kg/cm^2, is applied to this letter. The application of this pressure makes it possible simultaneously to cut from the transferable layer a pattern corresponding to the above-mentioned letter and to fix this pattern to the pressure-sensitive adhesive. The character is now withdrawn and the support of the transferable layer and the non-fixed parts of the film are removed.

The strip obtained is now covered (Figure 5) with a 50 mm wide and 25 microns thick transparent polyester strip 20.

A label is thus obtained which carries a black print on a white background and is of such rigidity that it can easily be introduced into holders for labels of a known type.

EXAMPLE 5.

6 parts of a butyl phthalate, 4.5 parts of carbon black, such as that sold under the trade name of "Carbon Black BL", 23 parts of a talc such as that sold under the trade name of Talc 10 M C T O, 0.3 part of a dispersing agent, such as that sold under the trade mark of "Pluronic" L 61, 2.8 parts of nitrocellulose, such as that sold under the trade name of Nitro-Cellulose E 130 and 64 parts of acetone are introduced into a malaxator.

The whole is malaxated until the nitrocellulose has dissolved completely, and is treated for 24 hours in a ball mill so as to obtain a very finely dispersed material.

The material thus obtained is then applied by means of a knife to a 25 microns thick polyester film so that after drying a transferable layer weighing 25 g/m^2 is obtained, carried by the polyester film, which forms its support.

A 50 mm wide strip is thereafter cut so as to obtain a transfer strip.

Secondly, a pressure-sensitive adhesive

strip is prepared by coating one of the faces of a 50 mm wide and 40 microns thick red polyvinyl chloride strip, by means of a knife, with an adhesive composition of the following constitution:

7.5 parts of a polyol-polyether having an OH number of 660, such as that sold under the trade mark "Caradol" G 3000;

35 parts of a resin consisting of an ester comprising colophony which has been esterified with glycerine, such as that sold under the trade name of Resolol G;

8.5 parts of a resin consisting of a triethylene glycol ester of hydrogenated colophony, such as that sold under the trade mark of "Staybelite" Ester 3;

11.5 parts of acrylic acid;

3 parts of stannous octoate, such as that sold under the trade name of T 9, as the catalyst; and

15.3 parts of tolylene diisocyanate such as that sold under the trade mark of "Suprasec" EN.

After polymerisation at 100°C the strip possesses a pressure-sensitive adhesive coating weighing 30 g per m².

It adhesive strength, measured on a steel plate in accordance with the AFERA standard specifications, is 300 centinewtons/cm, and its grab strength, also measured in accordance with the AFERA standard specifications, is 5 centinewtons/cm.

The transfer strip is applied to the adhesive face of the strip thus obtained in such a way that the transferable layer faces the adhesive, its support thus facing outwards.

A character as before and representing a letter 35 mm high and of about 630 mm² surface area is now placed on this support. A force of 70 kg is applied to this letter, corresponding to a pressure of about 11 kg/cm². The application of this pressure makes it possible simultaneously to cut from the transferable layer of the transfer strip a pattern corresponding to the abovementioned letter, and to fix this pattern to the pressure-sensitive adhesive. The character is now withdrawn, and thereafter the support of the transferable layer is removed, carrying with it the non-fixed parts of the transferable layer.

The strip thus obtained is covered with a 50 mm wide and 25 microns thick polyester strip.

A non-adhesive label is thus obtained which can be incorporated into a label carrier of a known type, and which shows black prints on a red background.

EXAMPLE 6.

2 parts of ethyl cellulose such as those sold under the trade name of Ethylcellulose N 300, 23 parts of talc, such as that sold under the trade name of Talc 10 M C T O, 4 parts of a yellow pigment, such as that sold under the trade name of Fast Yellow JN, 0.3 part of a dispersing agent such as that sold under the trade name of Pluronic L 61 and 70 parts of toluene are introduced into a malaxator. The whole is malaxated until the ethylcellulose has completely dissolved and is treated for 60 hours in a ball mill so as to yield a very fine material which is thereafter applied by means of a knife to a 25 microns thick polyester film so that after drying a transferable film weighing 20 g per square metre is obtained. The transferable layer is thus carried by a polyester film, which forms its support.

150 mm wide strip is now cut so as to give a transfer strip.

Secondly, a pressure-sensitive adhesive strip is prepared by coating one of the faces of a 150 mm wide and 100 microns thick black polyvinyl chloride strip, by means of a knife, with an adhesive solution of the following composition:

100 parts of a silicone adhesive as a 36% strength solution in xylene; and

1 part of benzoyl peroxide.

After drying, the strip possesses a pressure-sensitive adhesive coating weighing 30 g per square metre.

The linear adhesive strength of this strip, measured on a steel plate in accordance with the AFERA standard specifications, is 320 centinewtons/cm, and its grab strength, also measured according to the AFERA standard specification, is 90 centinewtons/cm.

The other face of the adhesive strip is covered with a pressure-sensitive adhesive of a usual type and this is covered with a release sheet intended to be removed at the time that the label is fixed.

The 150 mm wide transfer strip is applied to the adhesive face which has been left free, in such a way that the transferable layer faces the adhesive, its support thus facing outwards. A character suitably of plastic metal and representing a letter 80 mm high and of about 18 cm² surface area is now placed on this support, and a force of 200 kg, corresponding to a pressure of about 11 kg/cm², is applied to this letter. The application of this pressure makes it possible simultaneously to cut from the transfer strip a pattern corresponding to the abovementioned letter and to fix this pattern to the pressure-sensitive adhesive. The character is now withdrawn and thereafter the support of the transferable layer is removed, carrying with it the non-fixed parts of the layer.

The print obtained is now protected by covering it with a 150 mm wide and 25 microns thick transparent polyester strip of a known type, with the adhesive facing the print.

An adhesive panel is thus obtained which shows yellow patterns on a black background

and which can easily be fixed to a receiving surface after removing the release sheet.

EXAMPLE 7.

A 50 mm wide transfer strip is prepared in accordance with the method described in Example 6.

A pressure-sensitive adhesive strip is prepared by coating one of the faces of a 50 mm wide and 100 microns thick white polyethylene strip, by means of a knife, with an adhesive solution of the following composition:

100 parts of an acrylic copolymer such as that sold under the trade name of D 263 by Monsanto, as a 45% strength solution in a mixture of ethyl acetate and hexane;

5 parts of a 10% strength solution of sodium hydroxide in ethanol; and

50 parts of ethyl acetate.

After drying, the strip possesses a pressure-sensitive adhesive coating weighing 30 g per m^2.

The linear adhesive strength of this strip, measured in accordance with the AFERA standard specifications, is 60 centinewtons/cm.

The grab strength, measured according to the AFERA standard specification, is 10 centinewtons/cm.

The 50 mm wide transfer strip is applied to the adhesive face in such a way that the transferable layer faces the adhesive, its support this facing outwards, and a character according to Example 5 is applied (35 mm high—pressure 11 kg/cm^2).

The strip obtained is thereafter covered with a 50 mm wide and 25 microns thick known adhesive strip of transparent polyester, the adhesive facing the print.

A non-adhesive label showing yellow prints on a white background is obtained.

EXAMPLE 8.

A 50 mm wide transfer strip according to Example 6 is prepared, and a pressure-sensitive adhesive strip is prepared by coating one of the faces of a 50 mm wide and 125 microns thick transparent polyester strip with an adhesive solution of the following composition:

100 parts of a polyisobutylene having a molecular weight of about 100,000, such as that sold under the trade mark of "Oppanol" B 100;

10 parts of a polyisobutylene having a molecular weight of about 30,000, such as that sold under the trade mark of "Oppanol" B 3; and

500 parts of petroleum spirit "C" which is a mixture of normal iso and cyclo hydrocarbons and has a boiling point range between 70° and 100°C.

After drying, the strip has a pressure-sensitive adhesive coating weighing 25 g per m^2.

The linear adhesive strength of this strip, measured in accordance with the AFERA standard specifications, is 120 centinewtons/cm.

The grab strength, measured according to the AFERA standard specifications, is 40 centinewtons/cm.

The other face of the strip is coated with a pressure-sensitive adhesive of a known type and covered with a protective non-stick sheet.

The transfer strip is now applied to the adhesive face which has remained free, in such a way that the transferable layer faces the adhesive, its temporary support thus facing outwards, and a character as before is applied to this support in accordance with Example 5 (35 mm high—pressure 11 kg/cm^2).

The strip obtained is thereafter covered with a 50 mm wide and 25 microns thick polyester strip.

An adhesive label is obtained which shows yellow prints on a transparent background and can be fixed to a receiving surface after removing the protective non-stick sheet.

EXAMPLE 9.

A 150 mm wide transfer strip is prepared in accordance with Example 6, and a pressure-sensitive adhesive strip is prepared by coating one of the faces of a 150 mm wide white paper strip, weighing 70 g per m^2, with an adhesive solution of the following composition:

100 parts of a cis-1,4-polyisoprene sold under the trade mark of "Natsyn" 2200;

10 parts of a saturated resin of alicyclic hydrocarbon sold under the trade name of "Arkon" 125; and

500 parts of petroleum spirit "C", which is a mixture of normal iso and cyclo hydrocarbons and has a boiling point between 70° and 100°C.

After drying, the strip possesses a pressure-sensitive adhesive coating weighing 20 g per m^2.

The linear adhesive strength of this strip, measured according to the AFERA standard specifications, is 60 centinewtons/cm.

The grab strength, measured according to the AFERA standard specifications is 20 centinewtons/cm.

The transfer strip is then applied to the adhesive face as has been described in the preceding examples, and a character is then applied in accordance with Example 6 (80 mm high—pressure 11 kg/cm^2).

The strip obtained is covered with a 150 mm wide and 25 microns thick known strip of transparent adhesive polyester.

A paper label showing yellow prints on a white background is obtained.

EXAMPLE 10.

This example is described with reference to Figure 6.

3 parts of ethylcellulose, such as that sold

under the trade name of Ethylcellulose N 300, 8 parts of talc, such as that sold under the trade name of Talc 10 MCTO, 5 parts of a white pigment, such as that sold under the trade name of Synthecolor White 551, 6 parts of a wax, such as that sold under the trade mark of "Waxrex" Wax 31 E which is a microcrystalline wax comprising heavy isoparaffinic hydrocarbons, 10 parts of a resin, such as that sold under the trade name of Nevillac Soft which is a phenol modified coumorone-indene resin, 28 parts of methyl ethyl ketone, 21 parts of isopropanol and 18 parts of petroleum spirit "C" are introduced into a malaxator.

The whole is malaxated until the ethyl cellulose has dissolved completely and treated in a ball mill until a very fine material is obtained.

In order to produce a transfer strip 4, the material thus obtained is applied by means of a knife to the back of a 50 mm wide adhesive strip 6 (Figure 6) of a known type, the support of which consists of 30 microns thick metallised red polyvinyl chloride; the layer 5 deposited weighs about 25 g per m^2 after drying.

A 50 mm wide pressure-sensitive adhesive strip 3 is now applied to the layer 5 thus obtained, so that the adhesive 2 is in contact with the layer 5. The pressure-sensitive adhesive strip used consists of a 30 microns thick "Cellophane" support 1, coated with a pressure-sensitive adhesive 2 having an adhesive strength, measured according to the AFERA standard specifications, of 300 centinewtons/cm, and a grab strength of 5 centinewtons/cm, such as those described above.

A character 7 similar to that described in Example 1 and representing a letter 35 mm high and having a surface area of about 630 mm^2 is placed on the exposed face of the adhesive strip 3. A force of 70 kg, corresponding to a pressure of about 11 kg/cm^2, is applied to this letter and makes it possible simultaneously to cut from the transferable layer 5 a pattern corresponding to the abovementioned letter and to fix this pattern to the pressure-sensitive adhesive 2. Thereafter the character 7 is withdrawn and the adhesive strip 3, to which the cut pattern is fixed, is removed.

An adhesive label showing metallised red patterns on a white background is thus obtained.

EXAMPLE 11.

3 parts of ethylcellulose such as that sold under the trade name of Ethylcellulose N 300, 23 parts of talc such as that sold under the trade name of talc 10 MCTO, 5 parts of a blue pigment, such as that sold under the trade name of Synthecolour Blue 1025, 8 parts of a plasticiser, such as that sold under the trade name of Chlorinated Diphenyl DP 6, and 30 parts of isopropanol are introduced into a malaxator.

The whole is malaxated until the ethylcellulose has completely dissolved and treated in a ball mill until a very fine material is obtained, which is applied by means of a knife to one of the faces of a 70 microns thick film 6 (Figure 7) of fluorescent yellow polyvinyl chloride, so that after drying a transferable layer 5 weighing about 25 g per m^2 is obtained. The other face of the polyvinyl chloride film 6 (Figure 7) was coated beforehand with a layer 9 of a pressure-sensitive adhesive of a known type and is covered with a non-stick film 21.

A 50 mm wide strip is cut from the complex structure obtained.

An adhesive strip 3 is applied to the layer 5 in accordance with Example 10.

A character 8 representing a letter 35 mm high and of about 630 mm^2 surface area is placed on the exposed non-adhesive face of the adhesive strip 3 covering the layer 5. A force of 70 kg, corresponding to a pressure of about 11 kg/cm^2, is applied to this letter, making it possible simultaneously to cut from the transferable layer 5 a pattern 8^1 corresponding to the abovementioned letter, and to fix this pattern to the pressure-sensitive adhesive 2. Thereafter the character is withdrawn and the adhesive strip 2, to which the cut pattern 8 is fixed, is removed (Figure 7).

A transparent and colourless 50 mm wide adhesive strip 22 of a known type, the support of which consists of a 25 microns thick polyester, is now applied to the strip carrying an inscription 8^1, thus obtained, so as to form a protective film.

A pressure-sensitive adhesive label showing fluorescent yellow patterns on a blue background is thus obtained.

EXAMPLE 12.

A transferable material is prepared as in Example 11.

A 140 mm wide coating of material is applied to the non-coated face of a 150 mm wide pressure-sensitive adhesive strip having a transparent polyethylene support, in such a way as to leave a margin of 5 mm at each edge of the strip.

The coating is such that after drying a deposit of about 25 g/m^2 is obtained.

A 150 mm wide pressure-sensitive adhesive strip is applied to the coating in accordance with Example 11.

A character representing a letter 80 mm high and of about 18 cm^2 surface area is placed on the exposed face of the pressure-sensitive adhesive strip. A force of 200 kg, corresponding to a pressure of about 11 kg/cm^2, is applied to this letter, making it possible simultaneously to cut from the trans-

ferable layer a pattern corresponding to the abovementioned letter and to fix this pattern to the adhesive under pressure. Thereafter the character is withdrawn and the adhesive strip, to which the cut pattern is fixed, is removed.

A 150 mm wide transparent and colourless adhesive strip of a known type, whereof the support consists of a 25 microns thick polyester, is now applied to the strip carrying the print, so as to form a protective film.

An adhesive panel is thus obtained which carries transparent inscriptions on a blue background and shows transparent reserve areas at the top and bottom.

EXAMPLE 13.

A transferable material is prepared as in Example 11.

A 150 mm wide film 5^1 is formed by coating a 150 mm wide transparent polyethylene support 6^1. The coating is such that after drying a deposit of about 25 g/m² is obtained.

A 150 mm wide pressure-sensitive adhesive strip is applied to the coating in accordance with Example 11.

After applying a character to the exposed face of the pressure-sensitive adhesive strip and removing this adhesive strip, as has been described in Example 12, a transparent adhesive strip 23 with two faces 24, 25 is applied to the strip carrying the print (see Figure 8). The adhesive face 25 adheres to the exposed face of the layer 5^1 carrying the printed pattern, whilst the other adhesive face 24 is coated with a temporary non-stick film 26 which allows the label to be fixed at the time of use.

When using such a label, it suffices to remove the non-stick film 26 before applying the label to the surface which is to be labelled.

A panel carrying transparent inscriptions on a blue background is thus obtained.

When pressure is applied to the strip having the adhesive layer, the nature and appearance of the support of the transferable layer can be diverse. For example, in place of the printed supports such as described in Examples 10 to 13 it is possible to use supports of luminescent or irridescent colours, metallic supports, imitation wood supports, and various pigmented, coloured and printed supports, or wooden or metal supports, which make it possible to obtain printing effects which have hitherto been unachievable or difficult to achieve.

The adhesive layer preferably is sensitive to a pressure of between 5 and 30 kg/cm².

It may be noted from the various examples that the pressure sensitive adhesive may include an adhesive resin, a plasticiser and a filler. The adhesive resin may be selected from esters of colophony, petroleum resins, terpene resins, ketone resins, resin esters or their mixtures. Suitably the adhesive may include from 0 to 50% adhesive resin therein.

Furthermore it should be noted that the components of the adhesive label can be so chosen that the combination is very resistant to high temperatures, to radiations and to weathering.

The label can be produced in sizes which allow it is be used for road signs, and is useful for labels, panels, placards or any other surfaces carrying signs or indicative patterns.

In addition to its simplicity, the invention also has innumerable applications because of the variety of compositions obtainable.

It is to be understood that the invention extends to articles having surfaces marked by the method of the invention in addition to the method itself.

WHAT WE CLAIM IS:—

1. A method of making marked surfaces, said method comprising the steps of providing a first strip including a support having on at least one face a layer of a pressure sensitive adhesive substance having a grab strength of between 5 and 150 centinewtons per cm which bonds only in response to the application of pressure, placing a second strip including a support having on one face a transferable layer with said transferable layer in contact with but not bonded to said layer of adhesive, positively applying a pressure pattern through one of said strips corresponding to the desired markings whereby upon application of the pressure pattern the transferable layer is stuck to and effectively transferred to the adhesive, and then separating the strips.

2. A method according to claim 1 wherein the pressure pattern is applied to the strips through the second strip.

3. A method according to claim 2, wherein the support of the first strip has a layer of adhesive on two opposite faces, at least one of the layers having a release film removable after separation of the strips to allow adhesion of the first strip to an object.

4. A method according to claim 1 wherein the pressure pattern is applied to the strips through the first strip.

5. A method according to claim 4, wherein the support of the second strip has a layer of adhesive on a face other than the face having the transferable layer, the adhesive being covered by a release film.

6. A method according to any one of claims 1 to 5, wherein the support of the strip through which the pressure pattern is not applied is of wood or metal.

7. A method according to any one of claims 1 to 5, wherein the support of the transferable layer is of a material selected

from styrene polymers or copolymers, olefine polymers or copolymers, cellulosic derivatives, polyvinyl acetal, polyvinyl esters or polyvinyl halides, polyesters, polycarbonates and paper.

8. A method according to any one of Claims 1 to 5 or 7 wherein the support of the first and/or second strip is transparent.

9. A method according to any one of claims 1 to 8 wherein the support of the first and/or second strip is luminescent, iridescent, metallised, printed, pigmented or otherwise coloured.

10. A method according to any one of the preceding claims wherein a protective film is placed on said layer of adhesive to which the transferable image is adhered in said pattern after separation of said strips.

11. A method according to claim 10 wherein the protective film itself has a layer of adhesive with a further protective film which is removable.

12. A method according to any one of the preceding claims wherein after separation of the strips, a protective layer is applied to the second strip to cover the transferable layer.

13. A method according to claim 12 wherein the protective layer is covered with and adhered to a film having adhesive on both sides, and a further removable outer layer protects the adhesive on the side remote from the transferable layer.

14. A method according to any one of the preceding claims wherein the pressure-sensitive adhesive material forming the layer on the first strip is an adhesive compound selected from polyurethanes, silicones, crosslinked acrylic materials, polyvinyl ethers, natural rubbers, and synthetic rubbers or their mixtures.

15. A method according to claim 14 wherein the said adhesive material includes an adhesive polyurethane prepared from a mixture of at least one polyether-polyol of high OH number and at least one polyether-polyol of low OH number in such proportions that the average OH number of the said mixture is between 50 and 100, a polyisocyanate, a catalyst, and acrylic acid.

16. A method according to claim 14 wherein the said adhesive material includes acrylic materials crosslinked in the presence of agents chosen from peroxides, amines, metal cations or isocyanates.

17. A method according to claim 14 wherein the said adhesive material includes at least one adhesive silicone crosslinked in the presence of agents chosen from peroxides, amines or metal cations.

18. A method according to claim 14 wherein the said adhesive material includes at least one polyvinyl ether.

19. A method according to claim 14 wherein the said adhesive material includes natural and/or synthetic rubbers.

20. A method according to any one of claims 14 to 19 including an adhesive resin, a plasticiser and a filler in the said pressure sensitive adhesive material.

21. A method according to claim 20 wherein an adhesive resin in the said pressure sensitive material is selected from esters of colophony, petroleum resins, terpene resins, ketone resins, resin esters or their mixtures.

22. A method according to claim 21 wherein the amount of adhesive resin present in the pressure-sensitive adhesive is between 0 and 50%.

23. A method according to any one of the preceding claims wherein the pressure sensitive adhesive material forming the layer on the first strip is sensitive to a pressure of between 5 and 30 kg/cm^2.

24. A method according to any one of the preceding claims wherein the pressure sensitive adhesive material forming the layer on the first strip has a grab strength below 100 centinewtons/cm.

25. A method according to any one of the preceding claims wherein the pressure sensitive adhesive material forming the layer on the first strip has a bond strength of between 40 and 400 centinewtons/cm.

26. A method according to any one of the preceding claims wherein the said transferable layer is of a material including an organic polymer, plasticisers, fillers and/or pigments and/or waxes and resins other than the organic polymer.

27. A method according to claim 26 wherein the said organic polymer is selected from polyvinyl alcohols, polyvinyl ethers, polyvinyl acetates, copolymers of vinyl acetate and vinyl chloride, acrylic materials, nitrocelluloses, cellulose acetates, cellulose acetobutyrates, methylcelluloses, ethylcelluloses, carboxymethylcelluloses, styrene resins, polyurethanes and their mixtures.

28. A method according to claims 26 or 27 wherein the said plasticisers are selected from dibutyl phthalate, dicyclohexyl phthalate, dioctyl phthalate, chlorinated diphenyl, chlorinated triphenyl, tricresyl phosphate, and polyester plasticisers derived from sebacic acid or adipic acid.

29. A method according to claim 26, 27 or 28 wherein the amount of plasticisers in the said transferable layer is 30 to 300% of the amount of organic polymer.

30. A method according to Claim 26, 27, 28 or 29 wherein the said fillers are selected from dolomites, silicas, micas, chalks, titanium oxide, zinc oxide, starches and their mixtures.

31. A method according to any one of claims 26 to 30 wherein the said transferable film contains 2 to 11 parts of fillers and/or

pigments per one part of organic polymer.

32. A method according to any one of claims 26 to 31 wherein the pigments are inorganic, organic or metallic.

33. A method of making a marked surface substantially as hereinbefore described in any one of the foregoing examples.

34. An article having a surface marked by the method of any one of the preceding claims.

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1356426 COMPLETE SPECIFICATION
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

FIG.1

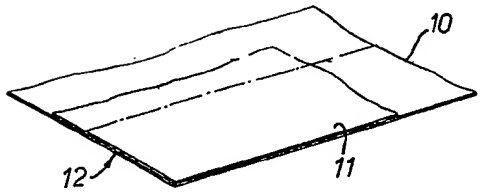

FIG.2

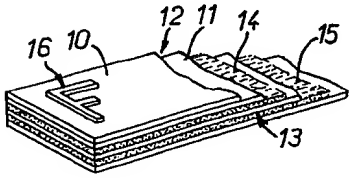

FIG.3

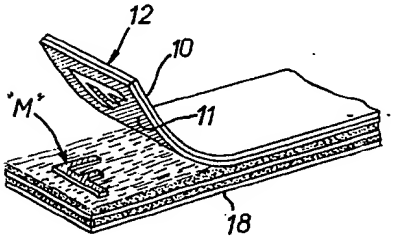

FIG.4

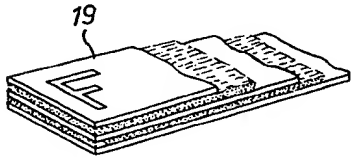

FIG.5

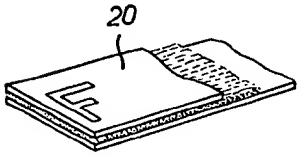

FIG 6

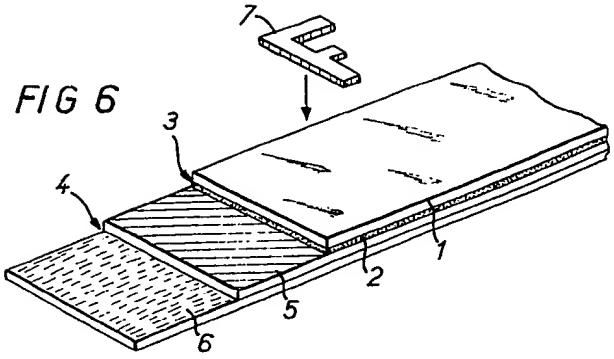

FIG.7

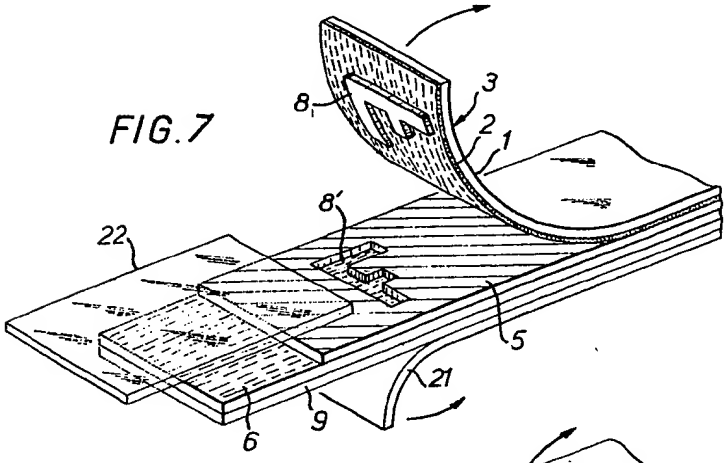

FIG.8